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THE OXIDATION OF ETHYL ALCOHOL BY MEANS OF POTASSIUM PERMANGANATE

DISSERTATION

PRESENTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE GRADUATE SCHOOL OF THE OHIO STATE UNIVERSITY

BY

JESSE ERWIN DAY

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The Oxidation of Ethyl Alcohol by Means of Potassium Permanganate.

I. Introduction.

It is a well known fact that the character and amounts of the oxidation products of both organic and inorganic substances with potassium permanganate as the oxidizing agent, are modified by the nature of the prevailing media in which the reaction takes place. The earliest recorded observations are those of Péan de Saint Gilles.[1] His results caused him to conclude that "high or low temperature, acid or alkaline media," frequently influenced the quality and the quantity of the reaction products. Margueritte, Pelouze, Bussey, Hempel and Berthelot arrived at similar conclusions as regards acidity and alkalinity. According to the first named investigator "if," *e. g.*, "we treat oxalic acid with potassium permanganate in the presence of sulfuric acid, carbonic acid and water are the only substances formed; but if potassium hydroxide is substituted for the mineral acid, no reaction takes place." Tartaric acid was converted into carbon dioxide, water and formic acid in acid solution, but only the two latter materials resulted when in an alkaline solution Sugar substances and lactic acid gave aldehyde and acetic acid in addition to carbon dioxide. In a subsequent paper[2] along the same lines, Péan de Saint Gilles was led to believe that the proportion of the reagent was also an influencing factor. Nine years later Chapman and Smith[3] wrote as follows: "If alcohol is treated with potassium permanganate and sulfuric acid, we obtain aldehyde and acetic acid, exactly as in the case of chromic acid. If, however, we employ a solution of crystallized permanganate, we obtain small quantities of aldehyde and acetic acid, together with various other bodies and oxalic acid. If the permanganate be rendered strongly alkaline with potassium hydroxide, no aldehyde and acetic acid whatever are produced." When the solutions were used hot, oxalic acid was the principal product; when cold, various other bodies probably identical with those obtained by Debus[4] in his oxidation of alcohol by nitric acid, were produced. Since that time similar investigations with ethyl alcohol have been carried on by different persons, the results of which are

[1] *Compt. rend.*, **46**, 808–11 (1858).
[2] *Ann. chim. phys.*, [3] **55**, 375 (1859).
[3] *J. Chem. Soc.*, **20**, 301–3 (1867).
[4] *Ann.*, **100**, 1–99 (1856).

not in complete harmony with each other, nor with those to which previous reference has been made. With but one exception (Chapman and Smith), acetic acid has been found in every case, regardless of whether the reaction occurred in neutral, acid or alkaline solution. Chapman and Smith[1] obtained oxalic acid as a reaction product when an aqueous solution of the crystallized potassium permanganate was used while others found it only when using an alkaline solution of this oxidizing agent. By means of the delicate protein-mineral acid test,[2] Voisenet[3] detected traces of formaldehyde as another reaction product, when the alcohol was oxidized by either chemical, physical or biological methods. Similar tests showed that the alcohol contained no traces of the aldehyde before being oxidized. A few of the chemical oxidizing substances employed were "manganic mixture," liquid oxygen and some of the oxides of nitrogen.

According to the results of Fournier,[4] an acetic acid yield of about 50% of the theoretical amount was possible when the oxidation was carried out in a 10% potassium hydroxide solution and at a temperature of 10° C. He obtained analogous results, with the exception of increased yield, when treating propyl, butyl, iso-butyl alcohols, etc., with potassium permanganate under similar conditions. In the case of ethyl alcohol, he did not determine the character and the amounts of the remaining 50% of the oxidation products, except to note that if acetaldehyde and ethereal salt were formed, they were in very small amounts. A few years ago, Denis[5] studied the action of potassium permanganate towards ethyl alcohol and acetaldehyde, both in the absence and presence of added caustic alkali. In a cold neutral aqueous solution he found acetic acid to be the sole reaction product with alcohol as the reducing agent. When the reaction took place in a cold alkaline solution (approximate strength = 5.4%), acetic acid was still the principal product, but carbonic and oxalic acids were also formed—"in larger amount the greater the concentration of the caustic alkali used." Witzemann,[6] quite recently, has made like observations on the oxidation of glucose by permanganate of potassium.

Morawsky and Stingl[7] noted the effect of temperature in addition to determining the nature of the product. They concluded that an increase in temperature merely promoted the rate of the reaction and that it had no effect on the nature and the amounts of the substance formed, a view

[1] *Loc. cit.*
[2] *Bull. soc. chim.*, **33**, 1198 (1905).
[3] *Compt. rend.*, **150**, 40–3 (1910).
[4] *Ibid.*, **144**, 331–3 (1907).
[5] *Am. Chem. J.*, **38**, 564 and 569–71 (1910).
[6] *J. Am. Chem. Soc.*, **38**, 151–161 (1916).
[7] *J. prakt. Chem.*, [2] **18**, 82–3 (1878).

which is not in accord with that of Péan de Saint Gilles. Hemmelmayr,[1] in his work on the spontaneous oxidation of sodium ethylate at ordinary temperature, obtained an acid distillate on the fractionation of the oxidation mixture with sulfuric acid. But at a temperature of 100°, a small amount of carbon dioxide was formed; and at 200° C., traces of oxalic acid were evident as a product additional to the other two acids. The amounts of carbon dioxide and oxalic acid were considerably increased at 210°. The acid distillate, on analysis, proved to be composed of formic and acetic acids. His results with sodium ethylate have been verified by Nef.[2] Hepter,[3] studying the action of potassium permanganate on organic compounds in acid and alkaline solution, found that substances having an alkyl group were always oxidized by alkaline permanganate to the corresponding aliphatic acid, carbon dioxide and oxalic acid, and the results were dependent upon the temperature of the reaction mixture and upon the position which the intermediate oxidation substance occupied in its own homologous series.

Barendrecht[4] determined alcohol in rather dilute solution by adding the alcohol to a boiling mixture of potassium permanganate and potassium hydroxide solutions, in which it is oxidized to carbon dioxide: $C_2H_5OH + 12KMnO_4 + 12KOH \longrightarrow 12K_2MnO_4 + 9H_2O + 2CO_2$. He noticed that the temperature was an essential factor in the complete conversion of the alcohol to carbon dioxide.

Cochenhausen,[5] on treating acetone with potassium permanganate in solution with potassium hydroxide found that it was oxidized to acetic, oxalic and carbonic acids. Greifenhagen, Koenig and Scholl[6] estimated carbohydrates, polyhydric alcohols, the corresponding aldehydes, ketones, and polysaccharides by oxidizing them to oxalic and carbonic acid with alkaline potassium permanganate. Greifenhagen found that the formation of oxalic acid and carbon dioxide was quantitative, and was dependent upon the alcohol, aldehyde and ketone groups.

Hitherto, definitely chosen conditions have not surrounded much of the experimental work on the oxidation of organic compounds by chemical substances. Among some of the more notable exceptions to the above statement should be included the work of Heimrod and Levene[7] on "Oxidation of Aldehydes in Alkaline Solution;" that of Kastle and Loevenhart[8] on the "Oxidation of Formaldehyde by Hydrogen Peroxide" and also

[1] *Monatsh.*, **12**, 1156–7 (1891).
[2] *Ann.*, **318**, 177 (1901).
[3] *Z. anal. Chem.*, **51**, 409–29 (1912).
[4] *Ibid.*, **52**, 167–72 (1913).
[5] *J. prakt. Chem.*, [2] **58**, 451 (1898).
[6] *Biochem. Z.*, **30**, 151 (1910); **35**, 169–193 (1911).
[7] *Biochem. Z.*, **29**, 31–59 (1910).
[8] *J. Am. Chem. Soc.*, **21**, 262 (1899).

that of Witzemann[1] in his investigation on "The Role of Atmospheric Oxygen in the Oxidation of Glucose with Potassium Permanganate in the Presence of Varying Amounts of Alkali." Nef[2] recorded the fact that in the oxidation of many carbohydrates in alkaline solutions, the amount of lactic acid formed varies in a remarkable way with the concentration of the caustic alkali used.

Among the objects of this investigation were the following: (1) to ascertain what are the reaction products when ethyl alcohol is oxidized both in neutral and in alkaline potassium permanganate solutions under known conditions of temperature; (2) to study the effect of temperature, of change in the initial concentration of the alkali present, and their combined effect on the character of the reaction products; (3) to study the mechanism of the oxidation of ethyl alcohol under these variable conditions.

II. Experimental Part.

(*a*) **Methods of Analysis.**—Throughout this work the ordinary qualitative methods were employed in the detection of *carbonic*, *acetic* and **oxalic acids.** In addition, oxalic acid was qualitatively obtained in well-defined crystalline condition as follows: the acid was first precipitated as the calcium salt by the method later described in the quantitative determination of same, filtered, washed and finally dissolved in dilute sulfuric acid. On the addition of a volume of absolute alcohol, about equivalent to that of the acid solution, the calcium salt of the last named acid passed out of solution, and was then removed. On spontaneous evaporation the free oxalic acid crystallized out in the form of beautiful needles. This procedure cannot be quantitative.

The presence or the absence of **formic acid** was determined by using a modification of the Jones method[3] on the neutralized acetic acid distillate, by making it alkaline with approximately 1.0 g. of sodium carbonate and adding potassium permanganate of known strength until a permanent pink color in moderately warm solution was obtained.

Carbon Dioxide.—The quantitative determination of this oxide was made by means of the Foulk apparatus.[4] A known portion of the solution under analysis was treated with the proper amount of hydrochloric acid and the carbon dioxide evolved, after having been conducted through a well cooled condenser and the appropriate drying agents, was absorbed by a caustic potash solution. A correction was applied for the amount

[1] *J. Am. Chem. Soc.*, **38**, 150–161 (1916).

[2] *Ann.*, **357**, 215; cf. *Ibid.*, **357**, 258 (1907).

[3] Compare *J. Am. Chem. Soc.*, **34**, 1091 (1912); *Am. Chem. J.*, **17**, 539 (1895); *Ber.*, **27**, 1061 (1894); *Ann. chim. phys.*, [35], **55**, 374 (1859); *Monatsh.*, **14**, 746 (1893).

[4] Foulk, "Notes on Quantitative Chemical Analysis," 1914 edition, p. 222.

of the carbon dioxide contained in the potassium hydroxide employed in the oxidations.

Oxalic Acid.—An aliquot part of the solution containing the oxidation products was used to determine the oxalic acid present as potassium oxalate. With phenolphthalein as the indicator the sample was first slightly acidulated with 20% acetic acid, boiled for a few minutes to drive off carbon dioxide, then made barely alkaline with ammonium hydroxide after which the oxalate was precipitated by 5% calcium acetate solution. The removal of the carbon dioxide was unnecessary but insured the absence of carbonate in the calcium precipitate. After filtering and washing the calcium oxalate on purified asbestos in a Caldwell crucible, it was titrated against standard potassium permanganate solution in the presence of 5% sulfuric acid in the usual manner. The filtration, washing and titration of the insoluble oxalate, when carried out as described, were found to be more rapid and satisfactory than when the precipitate was collected and washed on a filter paper, dissolved by means of sulfuric acid and then titrated.

Acetic Acid.—Methods were examined for the determination of this acid by the use of (1) hydrochloric acid, (2) sulfuric acid, (3) potassium hydrogen sulfate, (4) sirupy phosphoric acid, (*a*) distillation to approximately complete dehydration under reduced pressure, (*b*) distillation at ordinary pressure and maintaining the volume being distilled at 75 cc.

Some of these methods are discussed by Stilwell and Gladding,[1] particularly (4*a*). Withrow and Fritz[2] have modified the method of Stilwell and Gladding according to (4*b*).

The following additional facts were observed relative to these methods and their bearing on this problem: When proceeding according to (1) it was found necessary to add an excess of hydrochloric acid in order to sweep over the last portions of the acetic acid. By (2) and (3), sulfur dioxide was found present in the distillate, which introduced an appreciable error when the amount of oxalic acid in the oxidation solution was large. Carbon dioxide was present in the acetic acid distillate regardless of the method employed. When distilled with sirupy phosphoric acid under reduced pressure as in (4*a*), the solution of carbon dioxide in the condensate was avoided. Evans and Witzemann[3] have found that the loss of acetic acid by use of suction, was negligible when the acetic acid solution was very dilute. This was also the case in the experiments recorded in this paper. The distillation was much expedited by placing a second fractionating flask and a Kjeldahl connecting bulb between the distillation flask and the condenser, making it unnecessary to cool the contents of the distilling flask in order to prevent spattering on the addi-

[1] *J. Am. Chem. Soc.*, **4**, 105 (1882).
[2] Thesis by Howard Fritz of this laboratory.
[3] *J. Am. Chem. Soc.*, **34**, 1091 (1912).

tion of water to the hot mixture, as it was then extremely difficult for the phosphoric acid to reach the receiving vessel. The addition of water was made at the ordinary pressure in order to avoid the foaming, which otherwise occurred when the amount of alkali in the original sample was large. In (4*b*) the total volume of the distillate was not constant in quantity, as it was dependent upon the amount of acetic acid present in the sample. Inasmuch as the distillation was carried out at ordinary pressure, the carbon dioxide liberated was present in the condensate. Mr. Homer B. Adkins (this laboratory) found that bubbling carbon dioxide-free air through the distillate removed the undesirable gas without seriously affecting the quantity of acetic acid contained in these solutions of considerable dilution. In the following experiments on alcohol the same method was employed in eliminating the carbon dioxide. The distillate from methods (4*a*) and (4*b*) was titrated with a standardized potassium hydroxide solution with phenolphthalein as the indicator. In each experiment a correction was made for the volatile acids contained in the amounts of phosphoric acid used. It was observed in making these distillations that when the amount of potassium hydroxide present was large, a much greater excess of phosphoric acid over that required for the neutralization of the alkali, was necessary in order to completely expel the acetic acid, and also that the time required for the operation was decreased thereby.

(*b*) **Chemicals Used in the Oxidations.**—Absolute alcohol[1] was employed in these series of oxidations. Additional tests with phenyl-hydrazine and sodium hydroxide gave no turbidity, proving the absence of aldehydes. To obtain a pure product, commercial absolute alcohol was treated with calcium oxide in the customary way and then was stored with anhydrous copper sulfate in air-tight glass-stoppered bottles. In making up a standard solution sufficient alcohol (b. p. = 77.7° and 77.8°, at 739 and 749 mm.; $[d]_4^{20} = 0.7897$; $[d]_4^{25} = 0.7854$) was distilled from the copper sulfate to give a 2 *M* or 9.21% solution (92.096 g. anhydrous alcohol per liter of solution), having $[d]_4^{20} = 0.9830$ and $[d]_4^{25} = 0.9817$. These density values were referred to "Circular of the Bureau of Standards" No. 19, pp. 6 and 7, in order to get the per cent. by weight of alcohol present. An ordinary pyknometer (capacity about 60 cc.) was used in making these density determinations. All alcohol distillations were made in glassware, with cork connections.

Distilled water was aerated with carbon dioxide-free air for 5 to 6 hours. Carbon dioxide blanks were then run. One drop of 0.1017 *N* potassium hydroxide solution gave a permanent pink color to 100 cc. of the water containing one drop of phenolphthalein.

[1] Satisfying the requirements given in Merck, "Chemical Reagents, their Purity and Tests," 1914 edition.

The oxidizing power of the potassium permanganate was established by titrating samples of about 0.13 g. each in solution against standard potassium tetroxalate solution. It was found to have a value of 98.67% of that required by theory.

A potassium hydroxide solution containing 340.8 g. per liter (1 cc. = 0.004 g. carbon dioxide) was prepared and kept in a stock bottle.

(*c*) **Apparatus and Manipulation.**—Each oxidation which involved the addition of alkali was carried out as follows: The required amount of potassium hydroxide solution was measured into a wide-mouth, 2-liter balloon flask, and made up to 1000 cc. with carbon dioxide-free water. When the alkalinity was less than 5.32 g. per liter (*v.* Table IV) about 1100 cc. of solution was prepared and small portions were titrated against standard sulfuric acid, to avoid any error due to the extensive dilution of a small volume (0.14 to 8.5 cc.) of the potassium hydroxide stock solution. 30.404 g. of crystallized potassium permanganate, equivalent to 30 g. of 100% salt, was next introduced, and the flask immediately closed by a rubber stopper into which was fitted a mercury sealed glass stirrer, a 25 cc. pipet and a piece of ordinary glass tubing, for the oxidations carried out at 25° and 50°. For the series at 75° and 100°, in addition to the above, an ordinary condenser provided with a soda-lime guard-tube was attached through the stopper by means of two adapter tubes. The closed vessel was next clamped in position in a bath which was kept at the desired temperature

The thermostat bath was water for the 25° and 50° oxidations and paraffin for the 75° and 100° series. Heat was supplied by a large size "El Boilo" immersion heater. The amount of current flowing through the heater was automatically controlled by means of a mercury-toluene regulator and a lamp rheostat of considerable range. The temperature was held constant to within 0.15°.

When the desired temperatures of the flask and bath were reached and with the reaction mixture constantly stirred, 9.21% alcohol solution was slowly added drop by drop from a buret, loosely stoppered at the upper end, attached to the small glass tubing, until the reduction of the permanganate was complete. The end-point was determined by drawing a portion of the reaction mixture into the pipet, where, after the precipitated hydrated oxide or oxides of manganese had settled, the observations could be made. The color desired before discontinuing the addition of the alcohol in the case of the alkaline solutions was a very pale green, and in the neutral solutions was a delicate pink. This faint color was generally discharged within 24 hours through decomposition of the oxidizing agent.

The reaction mixture after being filtered in a carbon dioxide-free apparatus was made up to 2000 cc. and analyzed.

The 2-liter flask A containing the oxidation mixture was removed from the thermostat, placed on the rubber covered ring C and connected up as shown in Fig. 1. On the application of suction, and with the pinch-clamp F and screw-clamp H closed, the mixture was drawn from A into the

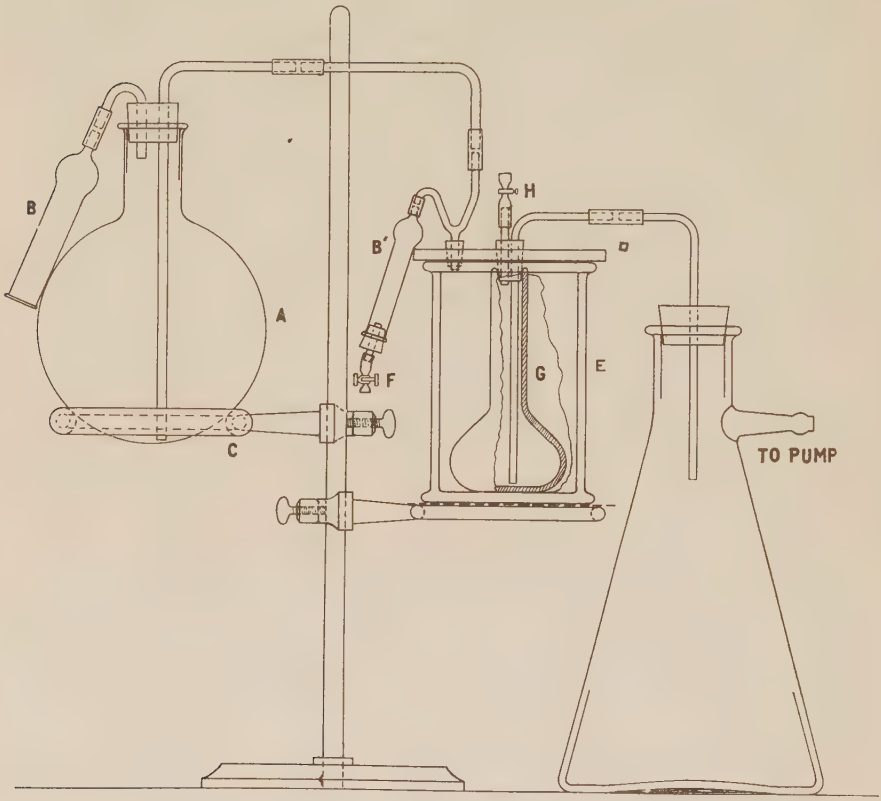


Fig. 1.

glass jar E. The oxide of manganese was retained on the outside of the Pukal filter G while the filtrate passed on into the 2-liter suction flask. After a sufficient amount of material had been transferred to E, the clamp F was opened to stop transference. When the filtration and washing were complete, clamp H was opened and water sucked into the cell to wash the inside of it. The plate glass cover D and the vessel were ground and coated with vaseline so as to prevent leakage of air into the apparatus. Several

types of filters were tried, but the unglazed cell was found to be highly satisfactory, as a clean filtration and three washings were usually completed within 10 to 15 minutes. The cell was cleaned by first removing the main portion of the precipitate with a steel spatula, then was sponged off and finally treated with hydrochloric acid after which water was sucked through it until the washings were free from chlorides. To assure myself that no appreciable error was introduced due to absorption or possible adsorption by the Pukal filter, determinations were made on a filtrate containing the maximum amount of oxidation products obtained in the experiment.

(*d*) **Data.**—The results obtained from 4 series carried out at 25, 50, 75 and 100° are given in Tables I, II, III and IV, respectively. They are also represented in the form of curves as found in Figs. 2, *et. seq.* 30.404 g. of potassium permanganate was used in each experiment.

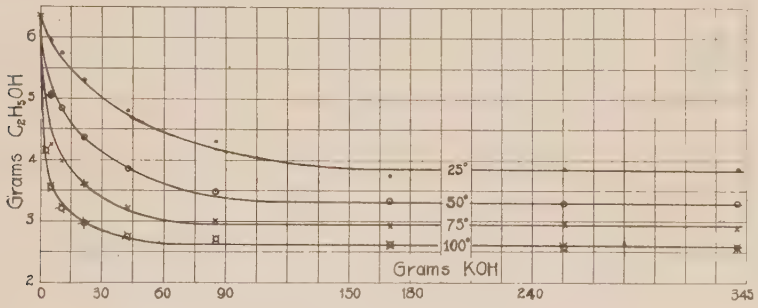


Fig. 2.

Oxidation Results.

Table I.

Temperature = 25°.

Col. 1. Expt. No.	Materials used. G. 2. KOH.	3. C_2H_5OH.	Found, with proper correction for CO_2 and CH_3COOH. G. 4. CO_2.	5. $(COOH)_2$.	6.	7. CH_3COOH.	Calculated for 4.605 g. alcohol. G. 8. CO_2.	9. $(COOH)_2$.	10. CH_3COOH.	11. % yield.
1	0.00	6.37	0.00	0.000	0.00	8.17	0.00	0.000	5.91	98.43
2	5.32	5.95	0.581	0.401	59.80	7.03	0.450	0.310	5.44	99.16
3	10.65	5.72	0.845	0.869	49.30	6.21	0.680	0.700	5.00	98.78
4	21.30	5.30	1.02	0.912	46.94	5.17	0.890	1.05	4.49	96.58
5	42.60	4.82	1.08	1.60	40.69	4.44	1.03	1.53	4.24	99.33
6	85.20	4.30	1.22	2.09	37.35	3.60	1.14	1.95	3.86	98.90
7	170.4	3.74	0.942	1.71	35.96	3.04	1.16	2.11	3.75	99.09
8	255.6	3.85	0.866	1.81	34.00	3.18	1.06	2.17	3.80	99.43
9	340.8	3.86	0.964	1.75	36.09	3.16	1.15	2.09	3.77	99.06

TABLE II.

Temperature = 50°.

	Materials used. G.		Found, with proper correction for CO_2 and CH_3COOH. G.				Calculated for 4.605 g. alcohol. G.			
Col. 1. Expt. No.	2. KOH.	3. C_2H_5OH.	4. CO_2.	5. $(COOH)_2$.	6.	7. CH_3COOH.	8. CO_2.	9. $(COOH)_2$.	10. CH_3COOH.	11. % yield.
10	0.00	6.40	0.00	0.00	0.00	8.17	0.00	0.00	5.87	97.76
11	5.32	5.05	1.04	1.07	50.00	4.99	0.95	0.98	4.55	97.48
12	10.65	4.77	1.39	1.64	46.30	4.02	1.34	1.58	3.88	97.42
13	21.30	4.37	1.45	1.96	43.22	3.33	1.53	2.06	3.51	98.74
14	42.60	3.85	1.49	2.12	41.71	2.50	1.78	2.53	2.99	98.13
15	85.20	3.48	1.33	2.15	38.78	2.09	1.76	2.84	2.77	97.68
16	170.4	3.35	1.32	2.18	38.13	1.96	1.81	3.00	2.70	98.89
17	255.6	3.30	1.35	2.24	38.12	1.84	1.88	3.12	2.57	98.82
18	340.8	3.30	1.32	2.10	38.90	1.98	1.84	2.93	2.77	99.61

TABLE III.

Temperature = 75°.

	Materials used. G.		Found, with proper correction for CO_2 and CH_3COOH. G.				Calculated for 4.605 g. alcohol. G.			
Col. 1. Expt. No.	2. KOH.	3. C_2H_5OH.	4. CO_2.	5. $(COOH)_2$.	6.	7. CH_3COOH.	8. CO_2.	9. $(COOH)_2$.	10. CH_3COOH.	11. % yield.
19	0.00	6.38	0.00	0.00	0.00	8.24	0.00	0.00	5.95	99.11
20	5.32	4.25	1.38	2.19	43.21	3.22	1.50	2.02	3.49	97.61
21	10.65	3.97	1.58	2.10	43.30	2.60	1.83	2.44	3.02	98.20
22	21.30	3.62	1.65	2.33	42.01	2.00	2.10	2.96	2.54	99.04
23	42.60	3.20	1.65	2.40	41.35	1.46	2.38	3.45	2.10	100.34
24	85.20	3.03	1.63	2.41	40.84	1.19	2.47	3.66	1.81	98.89
25	170.4	2.93	1.65	2.34	41.80	1.09	2.59	3.68	1.71	98.80
26	255.6	2.95	1.57	2.38	40.20	1.17	2.45	3.71	1.83	99.46
27	340.8	2.88	1.58	2.28	41.39	1.11	2.52	3.64	1.78	98.72

TABLE IV.

Temperature = 100°.

	Materials used. G.		Found, with proper correction for CO_2 and CH_3COOH. G.				Calculated for 4.605 g. alcohol. G.			
Col. 1. Expt. No.	2. KOH.	3. C_2H_5OH.	4. CO_2.	5. $(COOH_2)$.	6.	7. CH_3COOH.	8. CO_2.	9. $(COOH)_2$.	10. CH_3COOH.	11. % yield.
28	0.00	6.22	0.00	0.000	0.00	8.12	0.00	0.000	6.00	99.91
29	0.415	6.18	0.00	0.000	0.00	8.02	0.00	0.000	5.98	99.59
30	0.461	6.09	0.172	0.034	83.95	7.79	0.130	0.026	5.89	99.87
31	0.530	6.00	Undetd.	0.052	...	7.43	...	0.040	5.70	..
32	0.662	5.81	0.504	0.341	60.23	6.96	0.400	0.270	5.52	99.46
33	0.863	5.65	0.981	0.767	56.65	6.14	0.800	0.625	5.00	99.30
34	2.66	4.14	1.20	1.99	38.00	3.20	1.33	2.21	3.56	98.96
35	5.32	3.54	1.33	2.21	38.13	2.19	1.73	2.87	2.85	99.02
36	10.65	3.22	1.52	2.32	40.00	1.63	2.17	3.32	2.33	100.37
37	21.30	2.97	1.64	2.39	41.30	1.17	2.55	3.71	1.81	100.34
38	42.60	2.75	1.69	2.36	42.20	0.86	2.83	3.96	1.44	100.14
39	85.20	2.72	1.78	2.47	42.30	0.685	3.01	4.19	1.16	100.08
40	170.4	2.64	1.81	2.45	43.02	0.539	3.16	4.28	0.940	99.13
41	255.6	2.57	1.77	2.39	43.04	0.508	3.17	4.29	0.910	98.85
42	340.8	2.58	1.98	2.23	47.53	0.515	3.54	3.99	0.920	99.89

III. Discussion.

Fig. 2 shows the number of grams of absolute alcohol required to reduce a constant weight of potassium permanganate at the 4 different temperatures and with increasing initial concentrations of the alkali. Beyond an alkalinity of about 100 g. (cf. Fig. 10) per liter of water, an in-

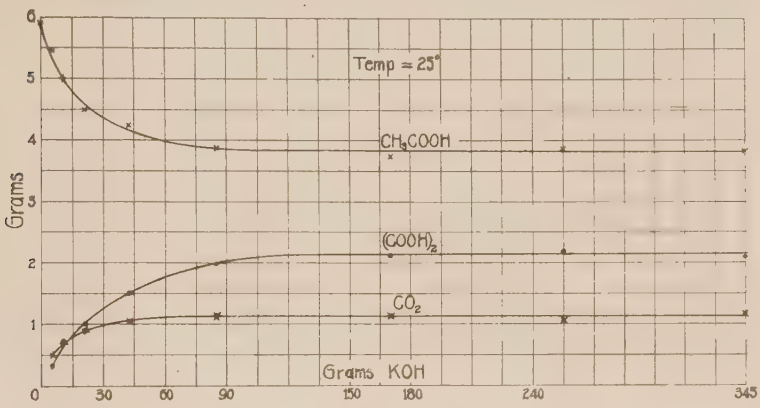


Fig. 3.

crease in the initial concentration of the potassium hydroxide had little further effect on the amount of alcohol necessary to reduce the potassium permanganate completely. The curves showing the amounts of the oxidation products in Figs. 3, 4, 5 and 6 are plotted on the basis of a constant quantity of alcohol (4.605 g. or 0.1 molecule). Figs. 7, 8 and 9 show the

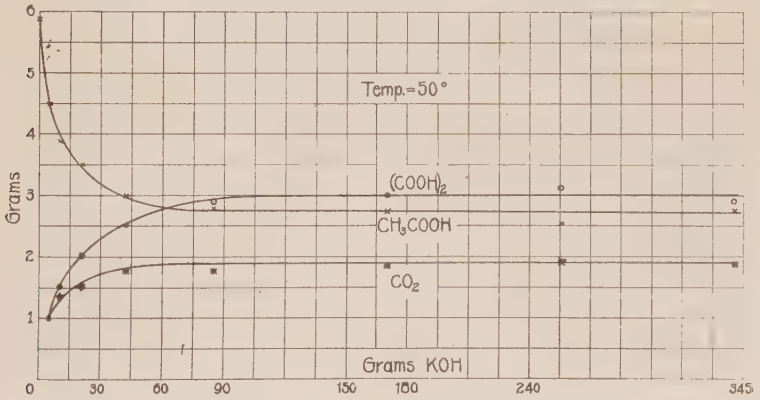


Fig. 4.

acetic, oxalic and carbonic acid curves for the 4 temperatures, respectively, and are represented on the same basis as those in the four preceding graphs.

(*a*) **Oxidation Products.**—In the neutral reactions, acetic acid was the only substance found in quantities estimable by the common analytical methods. Chapman and Smith[1] oxidized alcohol with alkaline potassium permanganate and obtained acetic aldehyde, acetic acid, "together with various other bodies and oxalic acid." The difference in my experiments between the yields of alcohol as accounted for in the form of oxidation products and 100% might, in some cases, be construed as

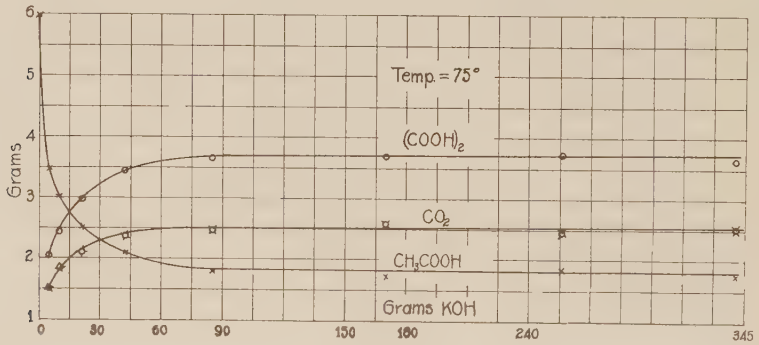


Fig. 5.

"various other bodies." The Jones test did not indicate any formic acid or formaldehyde. For a number of years the purity of alcohol has been determined by its oxidation to acetic acid by means of a chromic acid mixture.[2]

Mr. Homer B. Adkins[1] has shown that acetaldehyde is readily

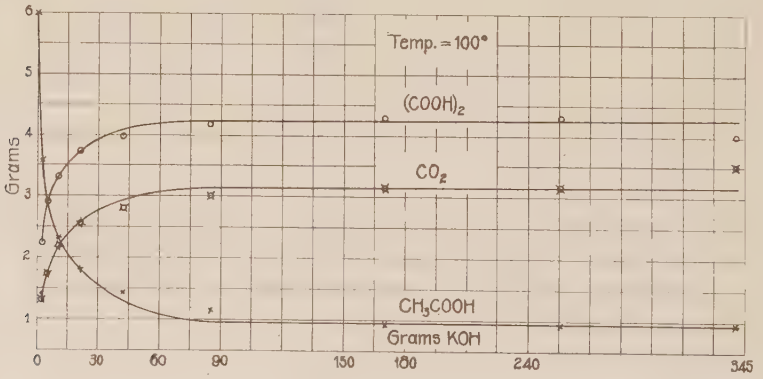


Fig. 6.

oxidized under the conditions used in this research. Hence, the amount of acetaldehyde, if present, must have been small. If other sub-

[1] *Loc. cit.*

[2] Chapman and Thorp, *J. Chem. Soc.*, **19**, 482–3 (1866).

stances than acetic acid were present, the amounts were too small to allow detection. Denis[1] obtained only acetic acid in her experiments. It is interesting to note that when Voisenet[2] oxidized alcohol with the oxides of nitrogen, he obtained formaldehyde as a product of the reaction.

The yields of alcohol accounted for as oxidation products (Col. 11, Tables I, II, III and IV) are between 97.42 and 100.37%. In general, the yields of the 100° experiments came nearer totalling 100% than any

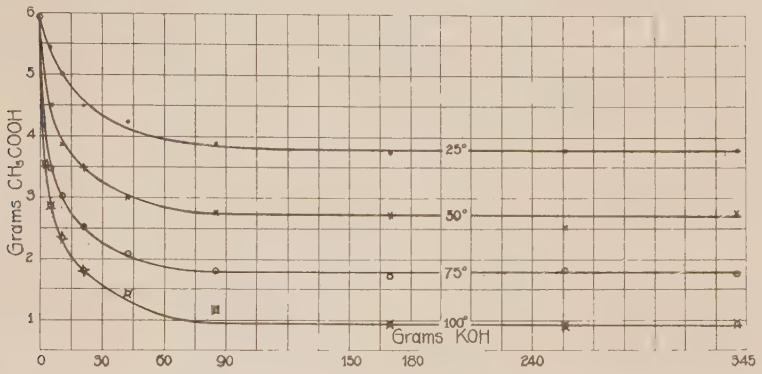


Fig. 7.

of the others. This does not necessarily mean that the 100° results should be accorded greater weight than the others. The low yield may have been due to incomplete oxidation or loss of the alcohol itself by evaporation from the reagent bottle. The latter is hardly possible because specific-gravity determinations of the alcoholic solution were made about every 5 days and at no time was there a difference of more than

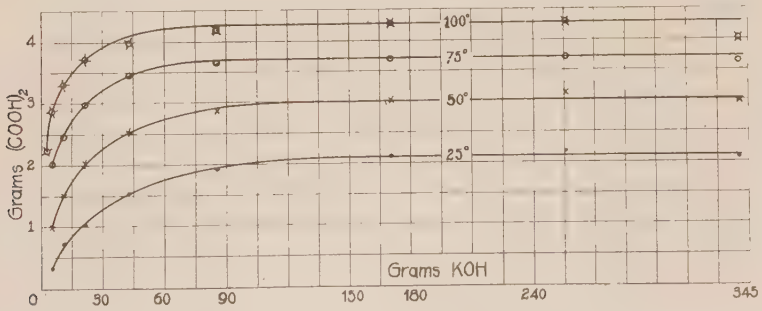


Fig. 8.

one or two in the fourth place. At the temperature of 75° and 160°, it was thought that there might be a slow but appreciable evaporation

[1] *Am. Chem. J.*, **38**, 564, 569–571 (1910).

[2] *Compt. rend.*, **150**, 40–43 (1910).

of alcohol while the drops were travelling from the end of the dropping tube to the oxidation mixture (a distance of 8–10 cm.). To check up this possibility, the dropping tube was extended below the surface of the mixture in the flask after which the repetition of all of the 75° series, and the last 5 of the 100° series, showed little or no difference in the amount of alcohol required for complete reaction from that used when the tube was of the shorter length.

Carbon Dioxide.—Only a trace was found in all the neutral experiments, and this was undoubtedly due to the unavoidable absorption of atmospheric carbon dioxide.[1] A correction for the carbon dioxide con-

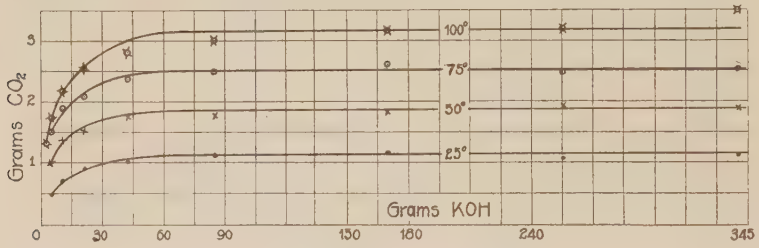


Fig. 9.

tent of the reagents was always made. Test experiments showed that the mercury seals on the stirrers were effective in preventing the circulation of the air.

The formation of carbon dioxide in the alkaline experiments might be attributed to the following causes: (1) oxidation of acetates or (2) formates formed in the reaction; (3) decomposition of the oxalates formed and subsequent oxidation; (4) oxidation of the intermediate compounds arising from the dissociation of the oxidation products of alcohol. That the presence of carbon dioxide cannot be due to the decomposition of the acetates is abundantly borne out by the many instances in the literature of the stability of acetates in alkaline potassium permanganate solutions. Chapman and Smith found that oxalates were also totally unaffected in boiling solutions of potassium hydroxide and potassium permanganate. When Barendrecht[2] substituted sodium hydroxide for potassium hydroxide in his analytical work he found acetic acid instead of carbon dioxide and that only one-third of the oxygen calculated for the latter named oxidation product had been utilized. Hence, the presence of the carbon dioxide cannot be due to any action between the acetates and oxalates and the alkaline potassium permanganate. Therefore, possibilities (1) and (3) are rigidly excluded.[3] The presence of car-

[1] Cf. Denis, *Am. Chem. J.*, **38**, 564, 571 (1907).

[2] *Loc cit.*

[3] Evans and Witzemann, *J. Am. Chem. Soc.*, **34**, 1096 (1912).

bon dioxide might be due to the intermediate formation of formates, as indicated by the work of Truchot,[1] who showed that formic acid is converted quantitatively into carbon dioxide in alkaline potassium permanganate solutions. Heimrod and Levene[2] explained the oxidation of acetaldehyde in alkaline solutions on the ground that formic acid is one of the reaction products. In view of the above facts, if formic acid is considered as an intermediate reaction product, it must be the decomposition product of a substance obtained from the acetaldehyde formed in the reaction. It will be shown below that it is not absolutely essential to postulate the formation of formic acid in order to account for the presence of carbon dioxide.

Oxalic Acid.—When the oxidations, with the exception of Expt. 30, were carried on in the presence of various initial concentrations of potassium hydroxide, oxalic and carbonic acids were formed with the acetic. Similar observations were made by Evans and Witzemann[3] in their experiments on the oxidation of propylene glycol, lactic acid, and pyruvic acid by means of alkaline potassium permanganate. Cochenhausen[4] also made similar observations in his work on the oxidation of acetone. Denis[5] found that acetic, oxalic and carbonic acids were the reaction products when alcohol is oxidized with alkaline potassium permanganate, a type of reaction which, in the present work, we have studied under definitely chosen conditions.

The formation of the oxalic acid may be due to the following possible causes: (5) oxidation of any acetates or (6) formates formed in the reaction; (7) oxidation of intermediate compounds formed from acetaldehyde. Denis[6] studied the effect of an excess of potassium permanganate on acetic acid in the presence of potassium hydroxide at 100°, and found that no reduction took place. Wanklyn and Cooper,[7] on heating acetates with a considerable excess of alkaline potassium permanganate at a temperature of 160–180° in the presence of manganese dioxide, obtained potassium carbonate. When manganese dioxide was not added, oxygen was evolved. Barendrecht[5] did not detect any reaction between boiling strongly alkaline permanganate and acetic acid. Sodium acetate, according to Lossen,[8] was partially converted into sodium oxalate when heated with sodium hydroxide, potassium permanganate and a small

[1] *Compt. rend.*, **63**, 274 (1866).
[2] *Biochem. Z.*, **29**, 49 (1910).
[3] *J. Am. Chem. Soc.*, **34**, 1086 (1912).
[4] *J. prakt. Chem.*, [2] **58**, 454 (1898).
[5] *Loc. cit.*
[6] *Am. Chem. J.*, **38**, 564 (1910).
[7] *Phil. Mag.*, [5] **7**, 138–140 (1879).
[8] *Ann.*, **148**, 174–6 (1869).

amount of water. Truchot[1] made the observation that potassium permanganate had no effect on acetic acid in the presence of potassium hydroxide. These facts indicate that oxalic acid is not formed by the oxidation of acetic acid.

Two drops of 0.089 *N* potassium permanganate solution were required to give a slight permanent color to the acetic acid distiliate when it had previously been made alkaline with sodium carbonate, indicating the absence of formic acid. A blank containing the same amounts of acetic acid and sodium carbonate needed but one drop to give a color of the same intensity. Had formic acid been one of the intermediate reaction products, it would have been immediately oxidized to carbon dioxide as shown above. Hence oxalic acid is not formed by the oxidation of formic acid. It is true, however, that formic acid has been oxidized to oxalic acid by means of nitric acid.[2]

It is apparent, therefore, that the oxalic acid is formed in alkaline solution from the reaction compound of acetaldehyde.[3] On the basis of this research and those of other investigators, this explanation must be accepted as the correct one.

Nef[4] and Denis[5] assume that the course of the reaction is as follows: Alcohol is dissociated into ethylidene and water.

$$CH_3.CH_2OH \longrightarrow CH_3.CH\begin{matrix}\nearrow \\ \searrow\end{matrix} + HOH;$$

the ethylidene is oxidized to ethylidene dihydroxide,

$$CH_3.CH\begin{matrix}\nearrow \\ \searrow\end{matrix} + 2HO \longrightarrow CH_3.CH(OH)_2 \longrightarrow CH_3.CHO + H_2O.$$

McLeod[6] has shown that acetaldehyde is converted into vinyl alcohol in the presence of alkali of a concentration of 0.10% or more; that is, the carbonyl group is enolized,

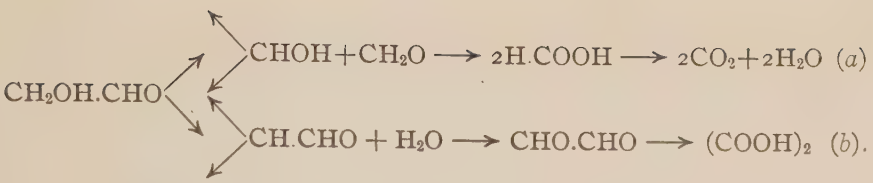
$$CH_3.CHO \longrightarrow CH_2 = CHOH;$$

the vinyl alcohol is then converted to glycollic aldehyde,

$$CH_2 = CHOH + 2HO \longrightarrow CH_2OH.CH(OH)_2 \longrightarrow CH_2OH.CHO + H_2O.$$

The glycollic aldehyde then undergoes a dissociation as expressed by the following:

[1] *Loc. cit.*
[2] Weyl, *Ber.*, **17**, 9 (1883).
[3] Homer Adkins (*Loc. cit.*).
[4] *Ann.*, **298**, 315, 319 (1897).
[5] *Am. Chem. J.*, **38**, 563–7 (1907).
[6] *Ibid.*, **37**, 25 (1907).



Such an interpretation would readily explain the presence of both oxalic and carbonic acids in alkaline solutions.

In this connection it is interesting to note that in the experiment of Denis[1] on the oxidation of ethyl alcohol in alkaline potassium permanganate solution, the ratio of the alcoholic equivalent of carbon dioxide to that of oxalic acid is as 12.6%: 7.6%, *i. e.*, the alcoholic equivalent of carbon dioxide is 62.5% of the total as carbon dioxide and oxalic acid. In the oxidation of acetaldehyde under approximately the same conditions the ratio of the acetaldehyde equivalent of carbon dioxide to that of oxalic acid is as 17%: 9.2% or the acetaldehyde equivalent of carbon dioxide is 64% of the total as carbon dioxide and oxalic acid. Col. 6 in the "Oxidation Results," gives similar information for my work on alcohol.

(*b*) **Effect of Variation of Initial Concentration of Alkali.**—This effect on the character of the oxidation products at 25, 50, 75 and 100° is shown in Figs, 3, 4, 5 and 6, respectively. In general, an increase in the initial concentration of the alkali causes an increase in the oxalic acid and carbon dioxide production, and a decrease in the acetic acid production. An examination of the curves shows that the yields of these acids reach approximately a constant value for a given temperature when the initial concentration of the alkali is about 100 g. per liter. The lowest initial concentration of potassium hydroxide employed at 25, 50 and 75° was 5.3 g. per liter. At this concentration oxalic acid and carbon dioxide were found at all 3 temperatures. At 100° the lowest possible initial concentration of alkali necessary for the production of oxalic acid in appreciable amounts was found to lie between 0.415 and 0.461 g. of potassium hydroxide (Expts. 29 and 30).

Kastle and Loevenhart[1] conclude that the "effect of bases on the rapidity of the oxidation is most remarkable." In their work, potassium and sodium hydroxide had practically the same effect; with ammonium hydroxide, the reaction was less.

Heimrod and Levene[1] give the following steps for the oxidation of acetaldehyde in alkaline solution: acetaldehyde → vinyl alcohol → glycollic aldehyde → glyoxal → formic acid and oxalic acid. In view of these facts it is apparent that the presence of formic acid does not necessarily explain the presence of carbon dioxide in these reactions.

If the mechanism of the oxidation of ethyl alcohol by potassium per-

[1] *Loc. cit.*

manganate in the presence of potassium hydroxide is properly expressed by Equations 1 to 5, inclusive, then the acetic acid-potassium hydroxide curves for equimolecular quantities of ethyl alcohol and acetaldehyde should be coincident. Furthermore, and simultaneously, the curves showing the ratio between the amounts of ethyl alcohol converted into oxalic acid and carbon dioxide should closely resemble similar ones for acetaldehyde. Within the limits of solubility, barium hydroxide was compared with caustic potash;[1] at first the barium hydroxide mixture reacted more rapidly, then both became the same. A similar effect was observed in these alcohol reactions, the rate of the reaction being roughly proportional to the concentration of the potassium hydroxide.

In Fig. 10 the logarithms of the acetic acid production are plotted against the logarithms of the initial concentration of the potassium hydroxide. The general equation for these lines is

$$y = \frac{B}{x^a}$$

where y is the concentration of the acetic acid obtained, x is the initial concentration of the potassium hydroxide, a is the tangent of the line and B is a constant. The values of a given below were obtained directly from Fig. 10 by measurement. To derive B we may use the equation

$$\log y = \log B - a \log x; \text{ thus,}$$

Temperature.	B.	a.
25°	6.74	0.1227
50°	6.20	0.1839
75°	5.41	0.2459
100°	4.74	0.3084

Knowing the values of B and a, it is easy to calculate the maximum alkali concentration which will still give the theoretical yield of acetic acid. This value was found to be as follows:

Temperature.	Alkali concentration.
25°	2.55
50°	1.19
75°	0.655
100°	0.460

As noted above, we found that the value at 100° must lie between 0.415 and 0.461 g., while the calculation shows that the amount of alkali is 0.46 g. These values mean that at any concentration of alkali greater than those given, acetic acid production will diminish and oxalic acid and carbon dioxide will begin to form.[2] It is therefore to be concluded that one of the marked effects of an increase in the alkali concentration must be to increase the concentration of vinyl alcohol.

It is evident that the results of any two oxidations at a given temperature will afford a means of obtaining both the value of a and the maximum

[1] Kastle and Loevenhart.

[2] McLeod, *Am. Chem. J.*, **37**, 24 (1907).

alkali concentrations that may be used in obtaining the theoretical yield of acetic acid. If y' and x' are the data obtained in a second oxidation, y the theoretical yield (*i. e.*, 6.003 g. of acetic acid), then x, the alkali concentration, may be calculated from the following equations:

$$\log y - \log y' = a\,(\log x' - \log x)$$

or

$$\frac{\log y - \log y' - a \log x'}{a} = -\log x.$$

(*c*) **Effect of Temperature.**—It was found that the temperature also has a twofold effect in these oxidations; namely, to increase the speed of the oxidation, and to modify the character of the reaction products. The general effect of temperature on the production of acetic, oxalic and carbonic acids, is shown in Figs. 7, 8 and 9, which shows that the acetic acid production falls off rapidly with the temperature while that of oxalic and carbonic acids increases with the temperature.

The fact that less alcohol was required for complete reduction at 100° (excluding neutral solution) than at the lower temperatures, means that more permanganate would have been required for the same amount of alcohol. In other words, the quantitative conversion of alcohol into oxalic and carbonic acids becomes more nearly complete at higher temperatures and in the presence of more of the oxidizing agent. Barendrecht employed a temperature of approximately 100° for his work. Kastle and Loevenhart found that an increase in temperature accelerated the reaction between formaldehyde and hydrogen peroxide.

Hetper[1] states that when ethyl alcohol is oxidized with alkaline potassium permanganate, the temperature requisite for a theoretical yield of acetic acid must be below 0°. This conclusion is not warranted, as can be seen from the discussion of Fig. 10, where it is shown that acetic acid is the only product formed with low potassium hydroxide concentrations.

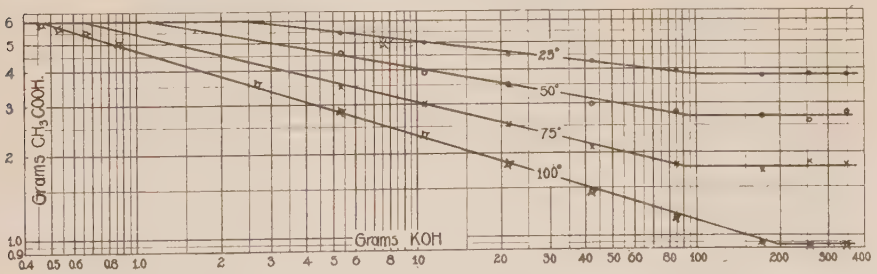


Fig. 10.

The fact that the logarithmic curves for acetic acid-potassium hydroxide are straight lines with but one sudden break is evidence favorable to the

[1] *Z. anal. Chem.*, **51**, 415 (1912).

explanation of acetic acid being the oxidation product of a simple and direct dissociation and oxidation product of the alcohol. Oxalic acid and carbon dioxide, when plotted on the same basis, did not give straight lines. When the natural logs to the base e of the respective acids were plotted against the 3rd root of the potassium hydroxide, a more or less straight line was the result, or the equation derived therefrom would have been of an order higher than one. This points to the formation of oxalic and carbonic acids as being due to two or more intermediate dissociations or reaction oxidations or probably both.

In Fig. 11 the tangents of the acetic acid log curves are plotted against temperature. A straight line passed through the 4 points cuts the Y-axis at a point near —25°. At this temperature the slope of the acetic acid curve is *zero*. If, *e. g.*, $x = 300$ when $a = 0$, by substitution in $\log B = \log y + a \log x$, the last term becomes zero, and $B = y = 6.003$, which is the theoretical yield in g. of acetic acid from 4.604 g. ethyl alcohol. This means that at the temperature indicated by the intersection of the line of tangents and the Y-axis the concentration of the alkali does not affect the theoretical yield of acetic acid.

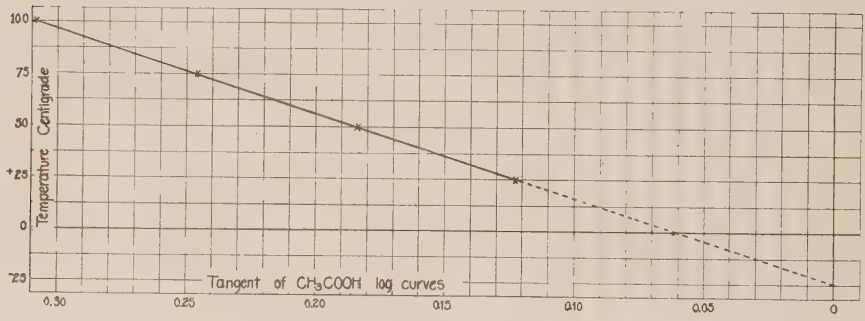


Fig. 11.

(*d*) **Oxides of Manganese.**—Approximately the same **color changes** recorded by Chapman and Smith[1] were observed in these series of oxidations, in alkaline and in neutral solutions. They stated "that the alkaline solution rapidly becomes green, and for a considerable time no binoxide of manganese is deposited," while it came down at once from the neutral solution. They made no reference to the weak alkaline solution. In this work it was noticed that these solutions remained pink for a very considerable length of time. In the case of the strong hydroxide solutions, a light coat of the brown oxide of manganese was found on the surface almost immediately following the addition of the reducing agent. The above workers were, without a doubt, correct in assuming the formation of the manganate. They thought, however, that this lower man-

[1] *Loc. cit.*

ganate modified the course of the reaction and used the oxidation of citric acid as an example of such a change. This last named compound, according to their work, reduced the permanganate to the manganate and then had no further effect on this second substance. Chapman and Smith considered the first reaction, in neutral solution, to take place as follows:

(6) $4KMnO_4 + 2HOH \longrightarrow 2K_2MnO_4 + 2HMnO_4.OH$,

(7) $2HMnO_4.OH \longrightarrow 2MnO_2 + 2HOH + 4O$,

thereby releasing two-thirds of the available oxygen without setting free any potassium hydroxide. Following the above changes, the solution first becomes acid, owing to the oxidation of the alcohol to acetic acid and later alkaline, through the action of water on the

(8) $2K_2MnO_4 + 2HOH \rightleftarrows 2MnO_2 + 4KOH + 2O$

potassium permanganate formed in Equation 6 which might result in a complicated series of products. The results of this work do not bear out their contention as acetic acid was identified as the only product of the reaction in neutral solution. At present, we generally think of the hydrolysis of the permanganate in the presence of the reducing agent as occurring in a manner somewhat different from that given above, namely,

(9) $4KMnO_4 + 10HOH \rightleftarrows 4KOH + 4MnO_2.2H_2O + 6O$.

The manganate and permanganate of potash are capable of selective oxidation. In the case of some organic compounds, it would seem that it is a matter of oxidation potential. Chapman and Smith held such an opinion in the oxidation of citric acid and Barendrecht's estimation of alcohol might be likewise interpreted. If alcohol as a selective reducing agent acts upon the permanganate in preference to the manganate then only reaction (9) need be given any attention. Further, from the following reactions:

(10) $3CH_3.CH_2OH + 6O \longrightarrow 3CH_3COOH + 3H_2O$,

(11) $3CH_3.COOH + {}_3\,3KOH \longrightarrow CH_3.COOK + 3H_2O$,

it is clear that there is an excess of one molecule of potassium hydroxide for every three molecules of acetic acid formed, assuming that the manganese is precipitated as the dioxide and that none of the potassium exists in combination with a complex oxide of manganese. Apparently either or both of these two assumptions are false in part or in their entirety as can be seen from the subsequent considerations: (1) Morawsky and Stingl[1] found potassium in combination with the hydrated oxide or oxides of manganese and assigned the formula $Mn_4KH_3O_{10}$ to the complex substance. If we accept their formula, then one atom of potassium (equivalent to one molecule of potassium hydroxide) enters into combina-

[1] *Loc. cit.*

tion as $Mn_4KH_3O_{10}$ for every four molecules of potassium permanganate undergoing hydrolysis. The removal of this molecule of potassium hydroxide plus the three neutralized by the acetic acid would leave the solution neutral, providing there was no other possible source of the hydroxyl ion. Any observed alkalinity in neutral oxidations might also be due to the hydrolysis of the potassium acetate. All reaction mixtures from neutral oxidations regardless of the temperature prevailing at the time of the oxidation, were alkaline to phenolphthalein and the intensity of the pink color of the indicator was of the same order as the temperature at which the experiments were carried out.

Some of the **precipitates** recovered from the oxidation of different alkalinity were of a different color while others varied merely in the shade of color. All of the residues from the neutral experiments were between a grayish black and a dirty brown in color and apparently without any relationship to the temperature factor. Those from strongly alkaline solutions were of a reddish brown appearance and those from mixtures of intermediate alkalinity were generally of a darker brown or coffee-brown color.

The first series of experiments conducted at 75° showed a decided break in the alcohol curve at a concentration of potassium hydroxide somewhere between the values of 170.4 and 255.6 grams. One series was carried on at an intended temperature of 10° but it was unsuccessful because of the difficulty encountered in maintaining the temperature constant at that value, hence was discarded. In addition, the substances undergoing chemical change were not agitated, which may not have placed them on a comparable basis with those that were being constantly stirred. One point worthy of mention in connection with the 10° series, is that a break similar to the above, but not quite so pronounced, was observed in the alcohol curve. It would seem that these two disruptions were due to decomposition of the permanganate, inasmuch as the oxidation products themselves at 75°, when calculated on the basis of 4.605 grams of alcohol, did not exhibit any such peculiarity. In this series solid potassium hydroxide was added to the one liter of 30% permanganate solution and when in large quantities, caused the local formation of a quantity of heat sufficient to raise the temperature of a portion of the solution much above that of the desired oxidation value. Simultaneously, a gaseous evolution was considerably in evidence. The low temperature series stood for approximately two months, hence the decomposition of the oxidizing material was aided by a time factor, although the amount of light which found its way to the reaction mixtures was small as they were in a refrigerator. When the order of the preparation of the alkaline oxidation mixture was modified, as described in II(*c*), the sudden breaks were absent as no appreciable heat of solution was thereby generated. According to

Abegg and Auerbach,[1] when potassium permanganate solution is treated with a concentrated potassium hydroxide solution, the solution is colored green and is accompanied by the evolution of oxygen.

$$(12)\quad 2KMnO_4 + 2KOH \rightleftarrows 2K_2MnO_4 + HOH + {}^1/_2O_2.$$

Technical caustic potash always contains small amounts of organic reducing materials which frequently are responsible for the green color. Brand and Ramsbottom[2], when using a 4% permanganate and a 20% potassium hydroxide solution, observed no green color at 100°. Sackur and Taegener,[3] on boiling a permanganate solution which contained more than an 8 *N* amount of the hydroxide always obtained oxygen evolution and the formation of manganate. According to Georg,[4] a double salt, $KMnO_4.K_2MnO_4$, is formed in alkaline solution of the two salts, which is soluble in a 20% potassium hydroxide solution without decomposition. The observations of Wanklyn and Cooper[5] indicate that the rate of the reduction of the potassium permanganate is decreased in the presence of alkali. One might anticipate such a result from the following considerations:

$$(13)\quad 2KMnO_4 + 2KOH \longrightarrow 2K_2MnO_4 + HOH + {}^1/_2O$$

$$(14)\quad K_2MnO_4 + HOH \longrightarrow 2KOH + MnO_2 + {}^1/_2O_2$$

The mass effect of the potassium hydroxide in strong alkaline solutions would then have a tendency to suppress, in some degree, reactions (13) and (14). As previously stated, however, the increased amount of the alkali seemed to hasten the reaction. Such an observation does not preclude the possibility of the effect of the potassium hydroxide, as it may be that the permanganate brings about the oxidation of the alcohol and not the manganate, as has been mentioned earlier in this article. One would expect the hydroxide to have the same influence on

$$(15)\quad 2KMnO_4 + HOH \longrightarrow 2KOH + 2MnO_2 + 1{}^1/_2O_2.$$

So far as could be ascertained, the rate of adding the alcoholic solution had no appreciable influence on the relative quantities of the oxidation products. This comparison could not be made very extensive at 100° because the addition of as much as 10 cc. of the solution caused the liberation of heat of reaction sufficient to raise the temperature of the paraffin bath as much as 3° C. Drop by drop addition of the alcohol allowed a maximum concentration, while larger amounts probably decreased the mass effect of the oxidizing material somewhat. Merezhkovskii,[6] in his investigation on the oxidation of the methyl groups of open-chain un-

[1] Handbuch d. anorganischen Chemie, IV, Part 2, 855.
[2] *J. prakt. Chem.*, [2] **82**, 336 (1910).
[3] *Z. Elektrochem.*, **18**, 718 (1912).
[4] *Compt. rend.*, **110**, 958 (1890).
[5] *Phil. Mag.*, [5] **6**, 288 (1878).
[6] *J. Russ. Phys. Chem. Soc.*, **46**, 1244–50 (1914).

saturated compounds, found that the strength of the potassium permanganate solution had a marked effect on the amounts of oxalic acid resulting. He obtained a maximum yield of oxalic acid with a 7% concentration of potassium permanganate and concluded therefrom that at this value the velocity of the oxidation of the methyl groups was equal to the velocity of the double union itself. Ethyl alcohol, of course, does not contain an unsaturated carbon linking, hence it is not likely to act as did the compound experimented with by the above investigator. Why he does it is not explained but Barendrecht emphasizes the use of a rapid delivery pipet when adding the alcohol to the oxidizing mixture. The inference is that the rate of reaction has some effect on the substance or substances resulting.

IV. Summary.

1. In neutral aqueous solutions of potassium permanganate at temperatures of 25. 50, 75 and 100°, the sole reaction product of the oxidation of ethyl alcohol is acetic acid.

2. (*a*) When ethyl alcohol is oxidized at the temperature of 25, 50 and 75° by means of alkaline potassium permanganate solution containing 5.32 to 340.8 g. potassium hydroxide per liter, the reaction products are acetic, oxalic and carbonic acids; (*b*) when ethyl alcohol is oxidized at 100° by means of potassium permanganate in the presence of 0.415 g. potassium hydroxide per liter of solution, the product is still acetic acid, but when the alkalinity was from 0.461 to 340.8 g. per liter. oxalic and carbonic acids were present in addition to the acetic acid.

3. The oxidation of ethyl alcohol by means of alkaline (*v.* Summary No. 2) potassium permanganate at the above temperatures is accompanied by a diminution in the yield of acetic acid and a corresponding increase in the yield of oxalic acid and carbonic acids as the concentration of the alkali was increased up to the beginning of the maximum effect.

4. (*a*) An increase in the temperature of the alkaline reaction mixture (excluding Expt. 29) diminishes the yield of acetic acid proportionately; (*b*) an increase in the temperature of the alkaline reaction mixture (excluding Expt. 29) increases the yield of oxalic and carbonic acids proportionately.

5. An increase in the temperature of the reaction mixture hastens the rate of oxidation.

6. An increase in the alkalinity of the reaction mixture, up to a certain maximum amount, increases the rate of oxidation.

7. A comparison between the results of two experiments recorded by Denis is given.

8. The rate of the addition of the alcoholic solution has no effect on

the relative amounts of the oxidation products so far as could be ascertained.

9. An equation has been developed for the relationship between the acetic acid production and the initial concentration of the alkali used when alcohol is oxidized at a given temperature in the presence of potassium hydroxide.

10. By means of this equation it is easy to establish the upper limit of the alkali concentration permitted and still obtain a theoretical yield of acetic acid, *i. e.*, the lower limit of alkali concentration at which oxalic acid forms.

11. By means of this equation it can be shown that at —25° the magnitude of the initial concentration of the potassium hydroxide used would not affect a quantitative yield of acetic acid.

12. An apparatus has been described for the filtering of sludge precipitates in the absence of the carbon dioxide of the air.

13. A description of the oxide (or oxides) of manganese sludges resulting from the reduction of potassium permanganate by means of ethyl alcohol both in neutral solution, and in solutions containing varying amounts of potassium hydroxide is given.

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